ISSN 1070-4272, Russian Journal of Applied Chemistry, 2013, Vol. 86, No. 9, pp. 1383−1387. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © N.V. Lakiza, O.I. Tissen, L.K. Neudachina, M.A. Ezhikova, M.I. Kodess, A.V. Pestov, 2013, published in Zhurnal Prikladnoi Khimii, 2013, Vol. 86, No. 9, pp. 1414−1418.

SORBENTS AND SEPARATION

Preparation of a Chelating Sorbent Based on Pyridylethylated Polyethylenimine for Recovering Transition Metal Ions

N. V. Lakiza[a], O. I. Tissen[a], L. K. Neudachina[a], M. A. Ezhikova[b], M. I. Kodess[b], and A. V. Pestov[b]

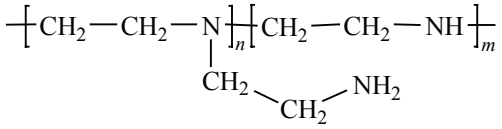
[a] *Yeltsin Ural Federal University, Yekaterinburg, Russia*
[b] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*
e-mail: pestov@ios.uran.ru

Received July 30, 2013

Abstract—A method was developed for preparing a chelating amino polymer, pyridylethylpolyethylenimine with maximal degree of substitution, by polymer-analogous transformations of branched polyethylenimine in reaction with 2-vinylpyridine. The ability of cross-linked pyridylethylpolyethylenimine with the degree of substitution of 0.32 to sorb Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, and Pb^{2+} ions present simultaneously in solution was evaluated. In an ammonium acetate sorption system (pH 3.5–4.0), the sorbent selectively interacts with Cu(II) ions.

DOI: 10.1134/S1070427213090114

Polymer-analogous transformations of macromolecular compounds allow the application fields of known and available polymeric materials to be considerably expanded. Polyethylenimine (PEI) is a commercially available and highly reactive polymeric matrix. The PEI reactivity is determined by its polybase properties caused by the presence of primary, secondary, and tertiary amino groups. In most cases, their ratio is 1 : 2 : 1 [1], but it strongly depends on the polymerization conditions:



The polybase nature of PEI ensures high ability of the macromolecule to form complexes with transition metal ions [2]. Sorbents can be jprepared both from unmodified cross-linked PEI [3–6] and from the functionalized polymer [6–12]. PEI as a polyamine is highly active in sorption of Hg(II) (3.3 mmol g^{-1} [3]), Cu(II), Ni(II), Co(II), and Zn(II) ions (no less than 2 mmol g^{-1} [6]) and, in combination with chitosan, in sorption of Hg(II) [4], Pt(IV), and Pd(II) ions [5]. Such complexing properties of PEI allow preparation of structure-forming [13, 14] and metal-containing catalytic [15] materials based on it. Additional N-functionalization of PEI, primarily occurring at the most reactive primary amino groups [10], significantly alters the sorption characteristics. For example, at pH < 2, the sorption capacity of PEI-based sorbents containing carboxylic acid residues for Cu^{2+} ions is 0.7 mmol g^{-1} [7, 8]. The sorbent prepared by introduction of the 2,3-dihydroxypropyl substituent exhibits high ability to sorb boric acid (>2 mmol g^{-1}) [9, 10].

In this study, we developed a procedure for PEI pyridylethylation, prepared sorption materials from the modified polymer, and evaluated their ability to sorb a series of transition metal ions.

EXPERIMENTAL

We used commercial branched polyethylenimine (Aldrich) with the average molecular weight of 25 kDa. 2-Vinylpyridine (Sigma–Aldrich) was distilled before use and stabilized with hydroquinone (0.05%). C,H,N analysis was performed with a Perkin–Elmer automatic analyzer. The IR reflection spectra were recorded with a Spectrum One spectrophotometer (Perkin–Elmer). The

^{1}H NMR spectra were taken with a Bruker DRX-400 spectrometer. Solution samples were dissolved in D_2O/DCl (10 mg mL^{-1}); DDS [sodium 3-(trimethylsilyl) propane-1-sulfonate] was used as internal reference. The solvent signal was suppressed by the presaturation method.

Synthesis of pyridylethylpolyethylenimine. A mixture of 5.4 g (0.024 mol of NH_2) of polyethylenimine, 2.16 mL (0.024 mol) of concentrated hydrochloric acid, 5.04 mL (0.048 mol) of 2-vinylpyridine, and 23.4 mL of water was kept for 10 min until a gelatinous mass formed. After that, the mixture was heated at 70°C for 24 h and then cooled. The polymer was precipitated from the mixture by adding 300 mL of acetone and then was reprecipitated two times more. The product was dried at room temperature to constant weight. Yield 6.4 g, degree of substitution 0.34.

The modification conditions and product characteristics are given in Table 1. The degree of substitution of the products was calculated from the ratios of the integral intensities of the ^{1}H NMR signals corresponding to the aliphatic and aromatic moieties.

Synthesis of sorbents. The sorbents were prepared by polymer cross-linking as follows. A 3.3-mL portion of epichlorohydrin was added with stirring to a mixture of 3.5 g of pyridylethylpolyethylenimine (degree of substitution 0.34), 20 mL of water, and 2.18 g of NaOH. The mixture was heated at 50°C for 2 h. The precipitate was filtered off, washed with water until the filtrate became free of Cl^- ions, and dried at 50°C to constant weight.

The ionization constants (pK_b) of functional groups of the sorbents were determined by potentiometric titration of separate weighed portions with a carbonate-free 0.05 M KOH solution (ionic strength μ = 0.1 M, KCl). The equilibrium was considered to be attained if pH of the solution over the sorbent ceased to change with time. The titration curves were plotted in the pH–V_t coordinates, and the apparent ionization constants of functional groups of the sorbent were calculated [16]. The static exchange capacity for hydroxide ions was determined by acid–base back-titration with potentiometric indication of the titration endpoint.

Standard solutions of transition metal nitrates were prepared by dissolving weighed portions of the corresponding analytically pure grade salts. The working solutions were prepared by diluting aliquots of the stock solution with distilled water. The solution acidity was maintained with an ammonium acetate buffer solution. The pH of the solutions was monitored with an ANION 4100 pH meter equipped with a combined glass electrode (ESK-10601). The sorption of transition metal ions present simultaneously in solutions was studied in batch experiments with intermittent stirring. The concentration of metal ions in the solution before and after the sorption was determined by flame atomic absorption spectroscopy with a Solaar M6 spectrometer. The degree of recovery of metal ions was calculated as the ratio of the difference between the ion amounts in the aqueous phase before and after the sorption to the initial amount of the ion in the aqueous phase.

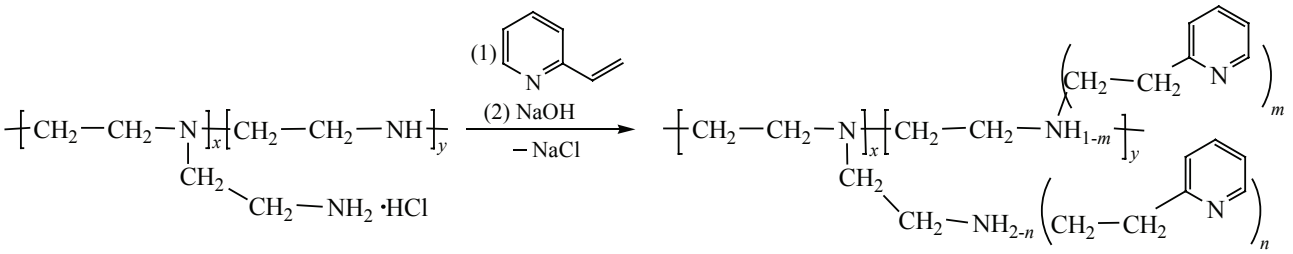
Table 1. Conditions of polyethylenimine 2-(2-pyridyl)ethylation and degree of substitution of the products (reaction time 24 h, 70°C)

Run no.	NH_2 : 2-vinylpyridine molar ratio	Polymer concentration, %	Degree of substitution
1	1 : 1	15	0.18
2	1 : 2	15	0.34
3	1 : 4	15	0.78
4	1 : 6.8	11	1.25
5	1 : 8	11	0.58

RESULTS AND DISCUSSION

High reactivity of PEI [17–22] is chiefly due to primary amino groups [10]. However, no attempts of PEI modification by the Michael reaction have been reported. It was shown previously that macromolecular amines (chitosan [23] and polyallylamine [24]) can be successfully involved into the reaction with 2-vinylpyridine to obtain new chelating derivatives [25]. Under the conditions of polymer-analogous transformations such as synthesis in a gel [26, 27], chitosan and polyallylamine behave as highly reactive polymeric nucleophiles. Here we used this approach for modifying polyethylenimine with 2-vinylpyridine.

Scheme 1. Pyridylethylation of polyethylenimine



The compositions and structures of the derivatives obtained were determined by elemental analysis and IR spectroscopy. New bands corresponding to pyridine ring vibrations appear at 1625, 1472, and 773 cm^{-1} against the background of strong PEI bands [3281 (N–H); 2934, 2813 (C–H); 1124, 1050 cm^{-1} (C–N)].

The conditions of polymer-analogous transformations and the degrees of substitution are given in Table 1. A 15% polymer solution, which was a gel, was kept at 70°C, because these conditions were shown previously to be the best for this reaction [23–25].

The incorporation of the 2-(2-pyridyl)ethyl group into PEI was confirmed by ^{1}H NMR spectroscopy. In the spectrum of pyridylethylpolyethylenimine (Fig. 1), there are signals in the interval 7.92–8.69 ppm, corresponding to hydrogen atoms in the pyridine ring and signals of methylene protons at 3.38 and 3.60 ppm, whereas signals of protons at the double bond of 2-vinylpyridine (6.07–6.52 ppm) are absent. No polymerization of 2-vinylpyridine was observed. The chemoselectivity (mono- or diaddition) could not be determined from the ^{1}H NMR spectra because of large signal width typical of macromolecular compounds. Taking into account the known reactivity of 2-vinylpyridine toward low- [28] and high-molecular-weight amines [23–25], we can assume that, with a successive increase in the degree of substitution, primary amino groups undergo pyridylethylation first, which is followed by pyridylethylation of secondary amino groups with the formation, in particular, of dipyridylethylated amino groups. Indeed, as follows from Table 1, at a twofold molar excess of 2-vinylpyridine (Table 1, run no. 2), the primary groups of PEI are fully functionalized. Further increase in the reagent excess (run no. 3) leads to involvement of secondary groups (both in the backbone and in pendant chains) into the reaction. Still larger excess (run no. 4) ensures complete functionalization of both primary and secondary amino groups of PEI. Tertiary amino groups of PEI do not participate in the reaction. An attempt to involve them into functionalization by further increasing the reagent excess (run no. 5) leads to a decrease in the degree of substitution, probably due to significant dilution of the reaction mixture, i.e., to a decrease in the polymer concentration, and to the occurrence of the reverse Michael reaction. Polyethylenimine is more reactive than chitosan owing to lower steric hindrance, but less reactive than polyallylamine because of

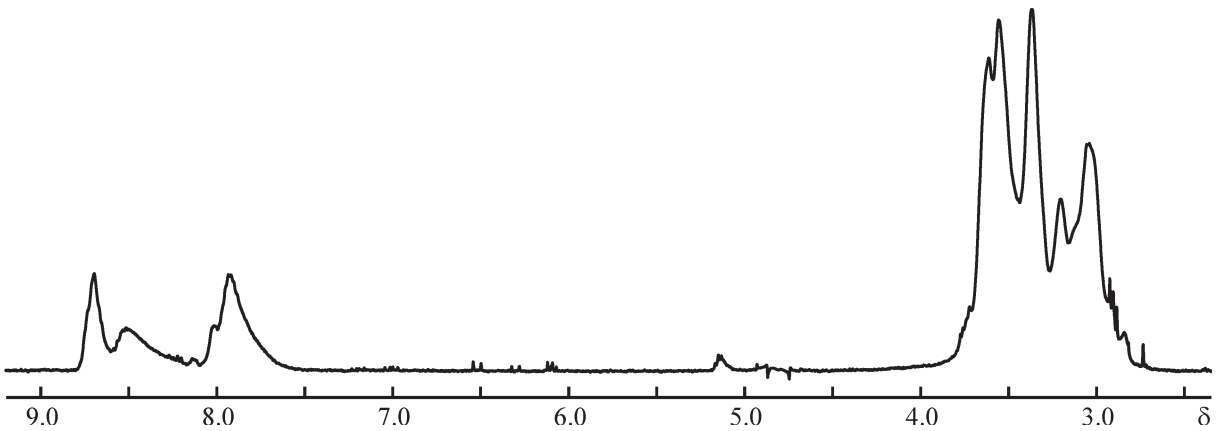


Fig. 1. ^{1}H NMR spectrum of polyethylenimine 2-(2-pyridyl)ethylation product. (δ) Chemical shift.

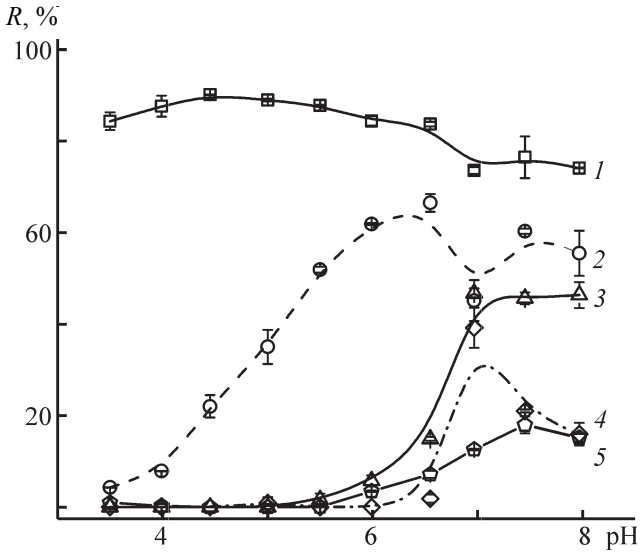


Fig. 2. Degree of sorption R of (*1*) Cu(II), (*2*) Ni(II), (*3*) Co(II), (*4*) Pb(II), and (*5*) Cd(II) ions as a function of pH of the ammonium acetate buffer solution. S1 sorbent, concentration of metal cations 0.1 mM.

the branched structure and presence of not only primary, but also secondary and tertiary amino groups.

Chelating sorbents based on pyridylethylpolyethylenimine were prepared by cross-linking of the polymer with epichlorohydrin. As follows from Table 2, SEC_{OH^-} increases insignificantly with an increase in the degree of substitution, which may be due to the combined effect of two factors: degree of cross-linking and hydrophilicity of the macromolecule. To calculate the apparent ionization constants of functional groups of the sorbents, we used the modified Henderson–Hasselbalch equation recommended for polymeric chelating sorbents [16, 29]. It follows from Table 2 that the calculated ionization constants of functional groups of pyridylethylated polyethylenimines are comparable with each other but differ from that of the monomeric analog, pyridine ($pK_b = 8.82$). This is due to the fact that introduction of alkyl substituents into the pyridine ring enhances its basicity owing to the positive inductive effect of the alkyl group. Similar explanation is suggested for the increased basicity of polyvinylpyridine sorbents in [16].

Table 2. Quantitative characteristics of sorbents based on pyridylethylpolyethylenimine

Sorbent	Degree of substitution, %	SEC_{OH^-}, mmol g^{-1}	pK_b
S1	32	5.40	7.22
S2	56	5.84	7.89
S3	80	5.87	7.38

We studied the sorption of simultaneously present Cu(II), Ni(II), Co(II), Zn(II), Mn(II), Cd(II), and Pb(II) ions from ammonium acetate buffer solution onto S1 sorbent. Its sorption capacity for Cu(II) ions varies with the acidity insignificantly and amounts to approximately 80%. The maximal sorption of Ni(II), Co(II), Pb(II), and Cd(II) ions is observed at pH 6.0–8.0. Zn(II) and Mn(II) ions are not recovered in the examined acidity range. The pH dependence of the recovery of the ions (Fig. 2) shows that the sorbent based on pyridylpolyethylenimine is selective to Cu(II) ions in the pH interval 3.5–4.0.

CONCLUSIONS

(1) A method was suggested for preparing pyridylethylpolyethylenimine using the gel procedure of polymer-analogous transformations. The product structure was determined, and relationships allowing preparation of polymers with different degrees of substitution were revealed.

(2) Cross-linked pyridylethylpolyethylenimine can be used as sorbent for selective separation of Cu(II) ions from Ni(II), Co(II), Zn(II), Cs(II), Mn(II), and Pb(II) ions in the pH interval 3.5–4.0.

ACKNOWLEDGMENTS

The study was supported by the program of the Ural Federal University for the support of young scientists within the framework of implementation of the Ural Federal University development program and by the Russian Federation President's grant MK-5745.2013.3.

REFERENCES

1. Dick, C.R. and Ham, G.E., *J. Macromol. Sci., Part A*, 1970, vol. 4, pp. 1301–1314.
2. Pshezhetskii, V.S. and Polinskii, A.S., *Vysokomol. Soedin., Ser. A*, 1981, vol. 23, pp. 246–254.
3. Freeland, G.N., Hoskinson, R.M., and Mayfield, R.J., *Environ. Sci. Technol*., 1974, vol. 8, pp. 943–944.
4. Kawamura, Y., Mitsuhashi, M., Tanibe, H., and Yoshida, H., *Ind. Eng. Chem. Res*., 1993, vol. 32, pp. 386–391.
5. Chassary, P., Vincent, T., Marcano, J.S., et al., *Hydrometallurgy,* 2005, vol. 76, pp. 131–147.
6. Takagishi, T., Okuda, S., Kurok, N., and Kozuka, H.,

J. Polym. Sci.: Polym. Chem. Ed., 1985, vol. 23, pp. 2109–2116.

7. Horváth, Zs. and Barnes, R.M., *Anal. Chem*., 1986, vol. 58, pp. 1352–1355.
8. Hughes, M.A., Wood, J., and Rosenberg, E.*, Ind. Eng. Chem. Res.,* 2008, vol. 47, pp. 6765–6774.
9. Mishra, H., Yu, C., Chen, D.P., et al., *Environ. Sci. Technol*., 2012, vol. 46, pp. 8998–9004.
10. Smith, B.F., Robison, T.W., Carlson, B.J., et al.*, J. Appl. Polym. Sci.,* 2005, vol. 97, pp. 1590–1604.
11. Fujiwara, K., Ramesh, A., Maki, T., et al., *J. Hazard. Mater*., 2007, vol. 146, pp. 39–50.
12. Ramesh, A., Hasegawa, H., Sugimoto, W., et al., *Bioresource Technol*., 2008, vol. 99, pp. 3801–3809.
13. Goon, I.Y., Zhang, C., Lim, M., et al., *Langmuir,* 2010, vol. 26, pp. 12247–12252.
14. Zhai, J., Zhai, Y., Wang, L., and Dong, S., *Inorg. Chem*., 2008, vol. 47, pp. 7071–7073.
15. Kidambi, S. and Bruening, M.L.*, Chem. Mater*., 2005, vol. 17, pp. 301–307.
16. Saldadze, K.M. and Kopylova-Valova, V.D., *Kompleksoobrazuyushchie ionity (kompleksity)* (Complexing Ion Exchangers), Moscow: Khimiya, 1980.
17. Gosselin, M.A., Guo, W., and Lee, R.J.*, Bioconjugate Chem*., 2001, vol. 12, pp. 989–994.
18. Peng, Q., Hu, C., Cheng, J., et al., *Bioconjugate Chem*., 2009, vol. 20, pp. 340–346.
19. Liu, J., Jiang, X., Xu, L., et al., *Bioconjugate Chem*., 2010, vol. 21, pp. 1827–1835.
20. Zaghloul, E.M., Viola, J.R., Zuber, G., et al., *Mol. Pharm*., 2010, vol. 7, pp. 652–663.
21. Alshamsan, A., Haddadi, A., Incani, V., et al., *Mol. Pharm*., 2009, vol. 6, pp. 122–133.
22. Zemek, J., Kuniak, L., Gemeiner, P., et al., *Enzyme Microb. Technol*., 1982, vol. 4, pp. 233–238.
23. Pestov, A.V., Bratskaya, S.Yu., Azarova, Yu.A., et al., *Zh. Prikl. Khim.,* 2011, vol. 84, no. 4, pp. 678–683.
24. Pestov, A.V., Lakiza, N.V., Tissen, O.A., et al., *Izv. Ross. Akad. Nauk, Ser. Khim.,* 2013, no. 12, pp. 1705–1710.
25. Bratskaya, S.Yu., Azarova, Yu.A., Matochkina, E.G., et al., *Carbohydr. Polym*., 2012, vol. 87, pp. 869–875.
26. Pestov, A.V., Zhuravlev, N.A., and Yatluk, Yu.G., *Zh. Prikl. Khim*., 2007, vol. 80, pp. 1184–1189.
27. Skorik, Y.A., Pestov, A.V., Kodess, M.I., and Yatluk, Y.G., *Carbohydr. Polym*., 2012, vol. 90, pp. 1176–1181.
28. Artamonov, A.A., Rozenberg, B.A., and Sheinkman, A.K., in *Reaktsii i metody issledovaniya organicheskikh soedinenii* (Reactions and Methods of Investigation of Organic Compounds), Moscow: Khimiya, 1964, vol. 14, p. 173.
29. Polyanskii, N.G., Gorbunov, G.V., and Polyanskaya, N.L., *Metody issledovaniya ionitov* (Methods for Studying Ion Exchangers), Moscow: Khimiya, 1976.